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Divergent Synthesis of Trifluoromethyl Sulfoxides and β-SCF_3 Carbonyl Compounds by Tandem Trifluoromethylthiolation/Rearrangement of Allylic and Propargylic Alcohols

Deng Zhu, Tong-Mei Ding, Hui-Yun Luo, Hua Ke, and Zhi-Min Chen*

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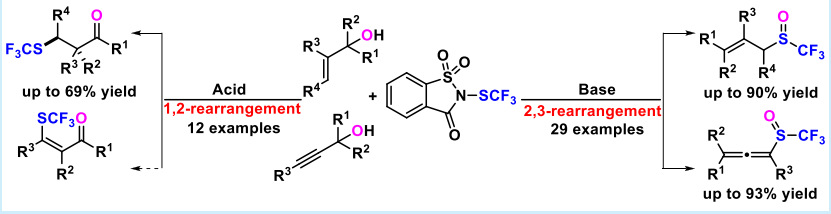

ABSTRACT: A selenium-catalyzed trifluoromethylthiolation/[2,3]-sigmatropic rearrangement of tertiary allylic and propargylic alcohols which could provide straightforward and facile access to trifluoromethyl sulfoxides was developed. Various allylic and allenic trifluoromethyl sulfoxides were obtained with moderate to excellent yields. Meanwhile, a Lewis acid mediated trifluoromethylthiolation/1,2-rearrangement to synthesize β-SCF_3 carbonyl compounds was also accomplished. These two tandem reactions feature with mild reaction conditions and metal-free. During these two reactions, the chemoselectivity of electrophilic trifluoromethylthiolation was revealed.

When compounds are introduced with fluorine-containing groups, they usually exhibit unique chemical, physical, and biological properties, which make them have a wide range of applications in the fields of pharmaceutical industry and agriculture.[1] Among them are $S(O)_nCF_3$-containing molecules (n = 0, 1, 2), which are in different oxidation states of sulfur atom show good electron-withdrawing character and exceptional lipophilicity, and these molecular structures are common in many drugs.[2] For instance, trifluoromethionine is a methionine derivative, fipronil is a highly active insecticide, and ponazuril is used as an antiparasitic molecule. On the other hand, compounds containing 1,1-diaryl skeleton are present in a number of bioactive natural products and pharmaceuticals (Scheme 1b).[3] Accordingly, it is important and necessary to explore modular routes for the efficient construction of $S(O)_nCF_3$-containing compounds[4,5] and organic molecules with 1,1-diaryl motifs,[6] and the methods for the synthesis of these two types of compounds have been widely developed, respectively. However, to the best of our knowledge, no example for the construction of γ,γ-diarylallyl trifluoromethyl sulfoxides which contain both of $S(O)CF_3$ and 1,1-diaryl groups and have broadly potential values has been documented (Scheme 1d), although Cahard and Shibata have reported the synthesis of allylic trifluoromethyl sulfoxides by [2,3]-sigmatropic rearrangement.[7] Therefore, the development of modular methods for the formation of γ,γ-diarylallyl trifluoromethyl sulfoxides is essential and in high demand.

Molecules containing an α-aryl ketone unit have shown many important biological activities (Scheme 1c) and have received much attention from synthetic chemists.[8] Some valuable strategies for the synthesis of them have been shown.[9] Among them, electrophilic semipinacol rearrangement of 1,1-diaryl allylic alcohols which could offer a direct route for the efficient synthesis of β-functional group α-aryl ketones has been successfully studied.[10,11] However, electrophilic trifluoromethylthiolation/semipinacol rearrangement of 1,1-diaryl allylic alcohols has not been reported although some related reactions have been discovered.[12] Inspired by the successful development of [2,3]-sigmatropic rearrangement and 1,2-rearrangement and combined with our research interest,[12c,13] we envisioned that the efficient construction of γ,γ-diaryl allyl trifluoromethyl sulfoxides by tandem trifluoromethylthiolation/[2,3]-sigmatropic rearrangement of 1,1-diaryl allylic alcohols and trifluoromethylthiolation/1,2-rearrangement of 1,1-diaryl allylic alcohols for the preparation of α-aryl β-SCF_3 ketones could proceed under appropriate reaction conditions (Scheme 1d). The development of a divergent synthesis strategy is a major goal in modern organic synthesis, which is

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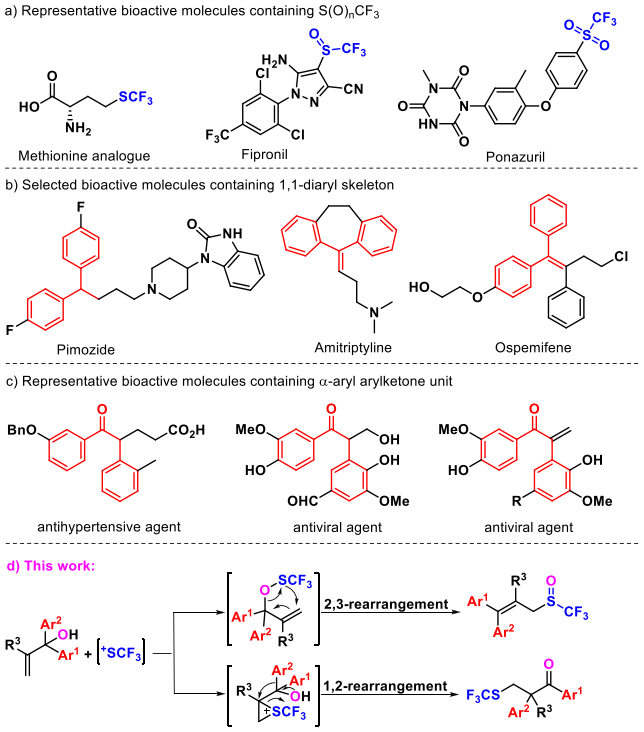
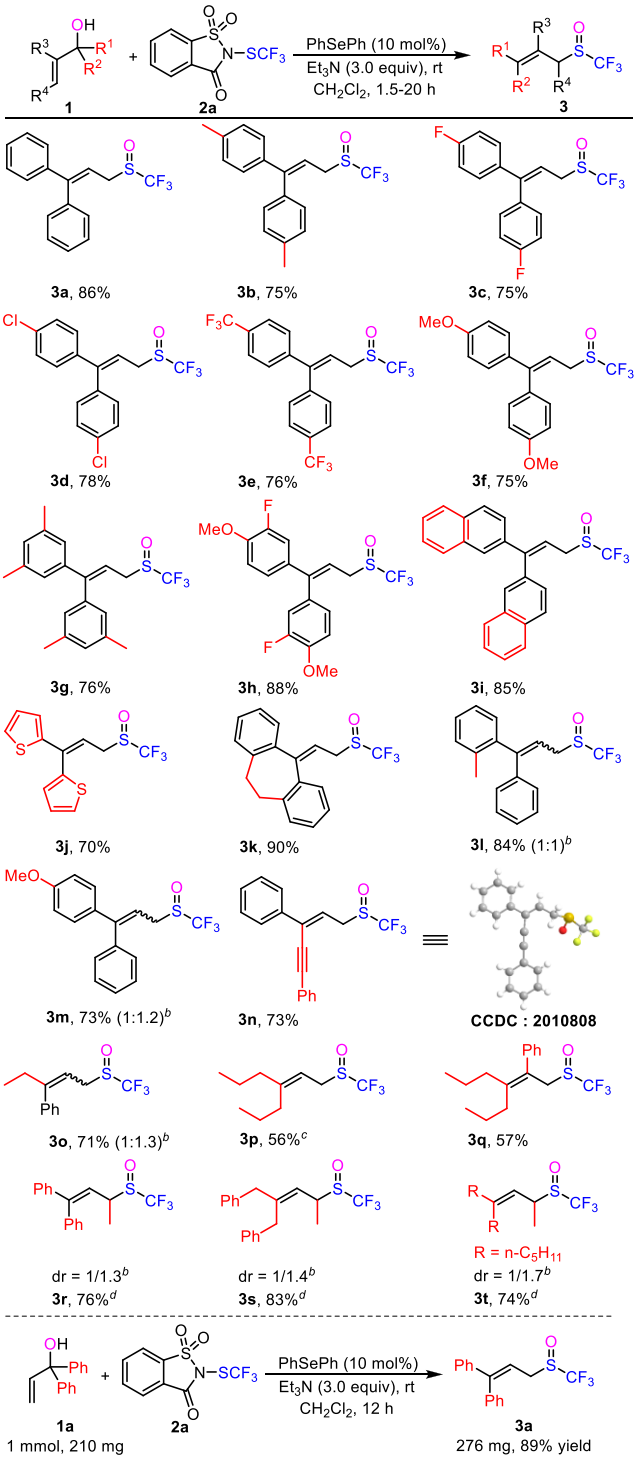
Scheme 1. Representative Bioactive Molecules and Synthetic Design



still highly desirable and challenging until now. For successful development of the divergent synthesis strategy, to realize the chemoselectivity of trifluoromethylthiolation (alkene vs hydroxy group) would be required. Herein, we report our preliminary results.

1,1-Diphenyl-2-propen-1-ol (**1a**) was first chosen as a model substrate to optimize the reaction conditions of the synthesis of *γ,γ*-diarylallyl trifluoromethyl sulfoxides. After careful screening, this reaction was found to be facile with 1.5 equiv of *N*-trifluoromethylthiosaccharin **2a** (Shen's reagent[5d]) in the presence of diphenyl selenide (PhSePh, 0.1 equiv) as a catalyst and triethylanmine (3.0 equiv) in dichloromethane at room temperature, and the desired product **3a** was obtained in 86% isolated yield (for details, see Table S1). It should be noted that the yield of **3a** was only obtained in 52% using Cahard's reaction conditions.[7b] Having determined the optimal reaction conditions for the synthesis of *γ,γ*-diarylallyl trifluoromethyl sulfoxide, the scope of various allylic alcohols was studied (Scheme 2). First, a series of substrates with the symmetrical groups on the aromatic ring were tested, and the corresponding products were obtained in moderate to good yields (**3b**–**k**). It was found that the reaction had good tolerance for the electrical properties of the groups (**3b**–**f**). Gratifyingly, substrates with multiple substituents on the phenyl group are suitable for the reaction system and gave the desired products with moderate to good yields (**3g**–**i**). To our delight, heteroaromatic and cyclic diphenyl compounds were well tolerated, producing the corresponding products in 70% and 90% yields, respectively (**3j**–**k**). Furthermore, substrates with unsymmetrical groups R^1 and R^2 were also subjected to the transformation. We found that the corresponding products were obtained with moderate yields and would have a certain *Z*/*E* ratio when groups R^1 and R^2 were different aryls (**3l**,**m**). Substrate with phenyl and ethyl

Scheme 2. Substrate Scope of Allylic Alcohols for the Synthesis of *γ,γ*-Diarylallyl Trifluoromethyl Sulfoxides[a]**



[a]Reaction conditions: unless otherwise noted, the reaction was conducted with **1** (0.1 mmol), **2a**[5d] (0.15 mmol), PhSePh (0.01 mmol), and Et_3N (0.3 mmol) in CH_2Cl_2 (2 mL) at room temperature under Ar. Isolated yield. [b]The ratio was determined by ^{19}F NMR. [c]The yield was determined by crude ^{19}F NMR using $PhCF_3$ as internal standard. [d]DMAP (0.2 equiv) was added in addition.

groups **1o** gave the similar result. It is worth noting that the single product **3n** was obtained with 73% yield using unsymmetrical allylic alcohol **1n** as the substrate and the

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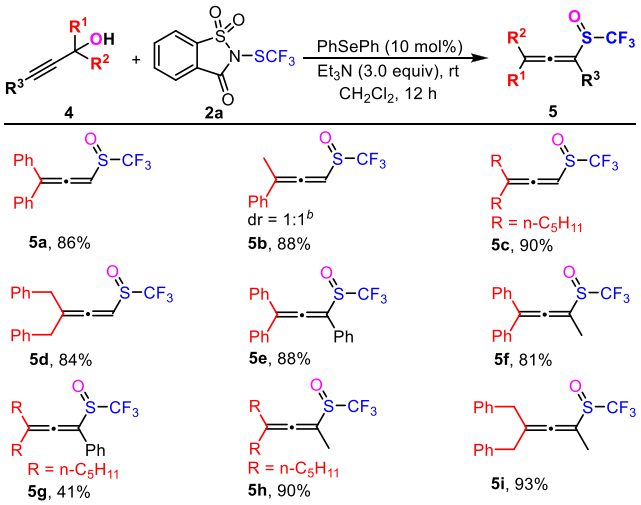
relative configuration of **3n** was assigned by X-ray crystallography. Substrates with the symmetrical alkyl groups were examined, and the reaction still proceeded smoothly albeit with lower yields than model substrate (**3p**,**q**). In particular, tetrasubstituted alkene product **3q** was rapidly obtained using **1q** as substrate. Finally, three different internal (*Z*)-alkene substrates (**1r**−**t**) were subjected to this system. Satisfactorily, the desired 2,3-rearrangement products were obtained with good yields but poor dr values. It should be noted that the products **3r**−**t** are easily to convert into the corresponding 1,3-dienes via elimination under acidic conditions at room temperature (for details, see the SI). To evaluate the utility of 2,3-rearrangement, a 1 mmol scale of **1a** was conducted. To our satisfaction, product **3a** was obtained with 89% yield.

Tandem trifluoromethylthiolation/[2,3]-sigmatropic rearrangement of propargylic alcohols which could provide direct approach to allenic trifluoromethyl sulfoxides, to the best our knowledge, has not been reported. In order to further broaden the scope of this reaction, some propargylic alcohols were also carried out under the standard reaction conditions. To our delight, the desired allenic trifluoromethyl sulfoxides were obtained with moderate to excellent yields (Scheme 3). The

Scheme 3. Substrate Scope of Propargylic Alcohols for the Synthesis of Allenic Trifluoromethyl Sulfoxides[a]

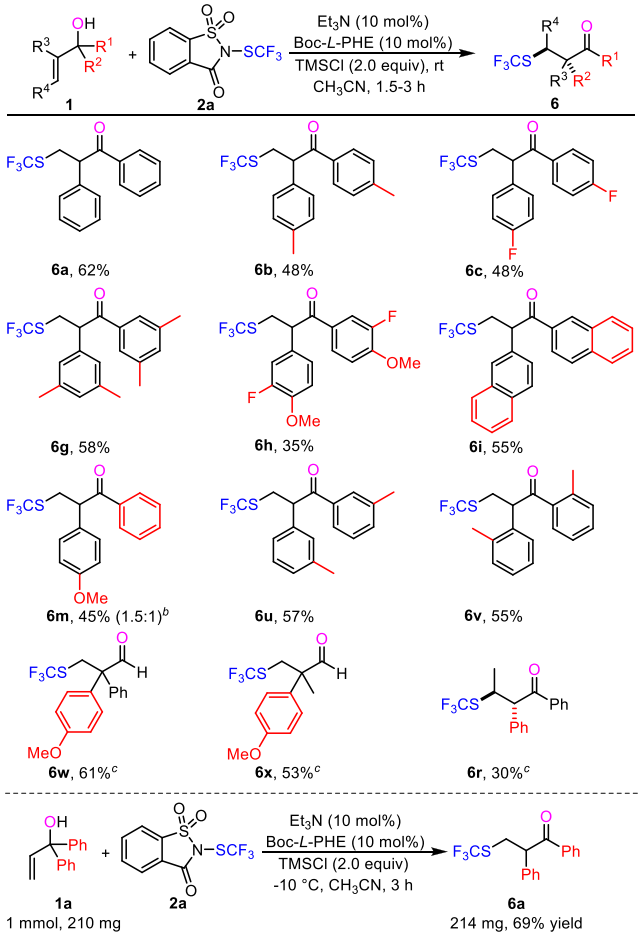


[a]Reaction conditions: unless otherwise noted, the reaction was conducted with **4** (0.1 mmol), **2a** (0.15 mmol), PhSePh (0.01 mmol), and Et_3N (0.3 mmol) in CH_2Cl_2 (2 mL) at room temperature under Ar. Isolated yield. [a]The ratio was determined by ^{19}F NMR.

use of unsymmetrical propargylic alcohol **4b** gave the product **5b** with diastereoselectivity ratio (dr = 1:1). Tetrasubstituted allene products were also rapidly produced using internal alkyne substrates (**5e**−**i**). Among them, because phenylacetylenyl alkyl alcohol **4g** could not be fully converted, product **5g** was obtained with only 41% yield.

Because 1,1-diaryl allylic alcohols are sensitive to strong acidic conditions and the migration ability of aryl group is relatively worse than the expansion ability of cyclobutanol, it is not easy to realize trifluoromethylthiolation/1,2-rearrangement of them. Actually, they are not suitable for the previous reaction system of allylic cyclobutanols which has been reported by our group.[12c] To further investigate 1,2-rearrangement and explore divergent synthesis strategy, we turned our attention to study trifluoromethylthiolation/1,2-rearrangement of 1,1-diaryl allylic alcohols. To our delight, the desired β-SCF_3 carbonyl compound **6a** was obtained with 62% yield when substrate **1a** was conducted with **2a** in the presence of triethylamine (Et_3N, 10 mol %), *N*-(*tert*-butoxycarbonyl)-L-phenylalanine (Boc-L-PHE, 10 mol %) and trimethylchlorosilane (TMSCl, 2.0 equiv) in CH_3CN at room temperature under Ar. It is worth noting that racemic compound **6a** was produced, although optically pure compound Boc-L-PHE was used (for details, see Table S2). With the optimized conditions in hand, the scope of 1,2-rearrangement was investigated with various allylic alcohols (Scheme 4). In general, the desired α-

Scheme 4. Substrate Scope of Allylic Alcohols for the Synthesis of β-SCF_3 Carbonyl Compounds[a]



[a]Reaction conditions: unless otherwise noted, the reaction was conducted with **1** (0.1 mmol), **2a** (0.15 mmol), Et_3N (0.01 mmol), Boc-L-PHE (0.01 mmol), and TMSCl (0.2 mmol) in CH_3CN (2 mL) at rt under Ar. Isolated yield. [b]The ratio was determined by ^1H NMR. [c]1 mmol scale under −10 °C.

aryl β-SCF_3 carbonyls were obtained with moderate yields. It was found that this 1,2-rearrangement system was sensitive to electrical properties of substrates. Electron-deficient substrate **1c** can give the product with 48% yield while substrate with 3-fluoro-4-methoxybenzene produced the product **6h** with 35% yield. It should be noted that the product of the preferential migration of electron-rich group was observed as the main product, which indicated that the reaction should be a cationic

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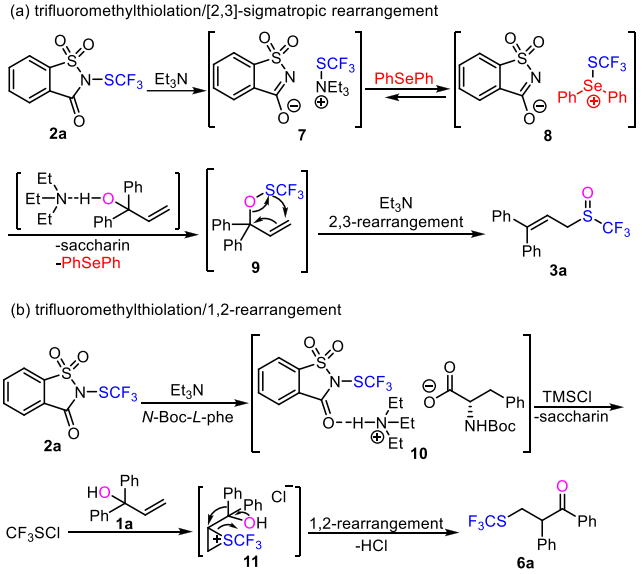
rearrangement process (**6m**).[9c] To our delight, the methyl group at different positions of phenyl group did not obviously affect the yield (**6u,v**). In addition, secondary alcohol substrates with 1,1-disubstituted alkene **1w** and **1x** were also relevant to this reaction, delivering rearranged products **6w** and **6x** with 61% and 53% yields, respectively. More importantly, quaternary carbon centers were readily constructed. Trisubstituted alkene substrate **1r** was applicable in this rearrangement and single product **6r** was afforded with 30% yield. The relative configuration of **6r** was determined by X-ray crystallography(for details, see the SI). Finally, we also tested propargylic alcohols, however, no desired 1,2-rearranged product was produced. Likewise, 1 mmol scale 1,2-rearrangement of **1a** was conducted, and **6a** was produced with 69% yield which is a little bit higher than 0.1 mmol scale.

Next, some additional experiments including ^{1}H and ^{19}F NMR investigations were performed to further understand these two rearrangements (for details, see the SI). On the basis of previous works[14] and our experimental outcomes, possible mechanisms for these two transformations are proposed in Scheme 5. For [2,3]-sigmatropic rearrangement, according the

Scheme 5. Proposed Mechanism



results of ^{19}F NMR, the species **7** could be first formed and the more active intermediate **8** could be generated in the presence of diphenyl selenide. The intermediate **8** fast reacts with hydroxy group of **1a** to form the species **9** with the assistance of triethylamine. The species **9** undergoes [2,3]-sigmatropic rearrangement to produce trifluoromethyl sulfoxide **3a** (Scheme 5a). The addition of diphenyl selenide accelerates the reaction rate. For 1,2- rearrangement, the species **10** is first generated in the presence of reagent **2a**, triethylamine, and Boc-L-PHE, which subsequently reacts with TMSCl to form compound CF_3SCl. The role of triethylamine and Boc-L-PHE may activate the e *N*-SCF_3 bond through a hydrogen-bonding interaction. Additionally, we speculated that triethylamine and Boc-L-PHE could act as buffer agents because 1,1-diaryl-2-propen-1-ol is perishable under strong acidic conditions. The active compound CF_3SCl reacts with the alkene moiety of **1a** to give trifluoromethyl-substituted thiiranium ion intermediate **11**. The intermediate **11** undergoes *anti* 1,2-migration and deprotonation to deliver product **6a** (Scheme 5b).

In summary, a tandem trifluoromethylthiolation/[2,3]-sigmatropic rearrangement of tertiary allylic alcohols and propargylic alcohols was disclosed, which required using diphenyl selenide as catalyst to achieve moderate to excellent yields with these two new substrates. Among them, tandem trifluoromethylthiolation/[2,3]-sigmatropic rearrangement of propargylic alcohols was discovered for the first time. These outcomes may give some new insight of selenium catalysis. Meanwhile, an electrophilic trifluoromethylthiolation/1,2-rearrangement of 1,1-diaryl-2-propen-1-ols was also explored. This result required adding triethylamine and Boc-L-PHE to overcome 1,1-diaryl-2-propen-1-ol deterioration. A divergent synthesis strategy was successfully developed by simply regulating the reaction conditions. These two tandem reactions provide facile access to trifluoromethyl sulfoxides and β-SCF_3 carbonyl compounds. Various trifluoromethyl sulfoxides and β-SCF_3 carbonyl compounds were diversely synthesized with moderate to excellent yields. The catalytic asymmetric manner of these two reactions is being studied in our lab.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02875.

Experimental procedures, characterizations and analytical data of products, and NMR spectra (PDF)

Accession Codes

CCDC 2010808 and 2032082 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Zhi-Min Chen − *School of Chemistry and Chemical Engineering, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs and Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P.R. China;* orcid.org/0000-0002-6988-8955; Email: chenzhimin221@sjtu.edu.cn

Authors

Deng Zhu − *School of Chemistry and Chemical Engineering, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs and Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P.R. China*

Tong-Mei Ding − *School of Chemistry and Chemical Engineering, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs and Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P.R. China*

Hui-Yun Luo − *School of Chemistry and Chemical Engineering, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs and Frontiers Science Center for Transformative Molecules, Shanghai Jiao Tong University, Shanghai 200240, P.R. China*

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Hua Ke − *Engineering Technology Research Center for Environmental Protection Materials, Pingxiang University, Pingxiang, Jiangxi 337055, P.R. China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c02875

Notes

The authors declare no competing financial interest.

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